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FLOURINE-CONTAINING COPOLYMER AQUEOUS DISPERSION COMPOSITIONS
WHICH ARE CROSSLINKABLE AT AMBIENT TEMPERATURE

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Abstract

Problem

To provide coating films with excellent low-temperature film formability, external appearance, strength, stain resistance, boiling water resistance, solvent resistance, weather resistance, and adhesion to substrates.

Means to solve the problem

The present invention can be solved by the seed polymerization of a mixture of monomers comprising specific amounts of an acrylic acid alkyl ester and/or methacrylic acid alkyl ester and an ethylenically unsaturated monomer in the presence of fluorine-containing polymer particles; the fluorine-containing copolymer compositions of the present invention contain (1) a fluorine-containing polymer aqueous dispersion containing a specific amount of active carbonyl group-containing ethylenically unsaturated monomer and (2) a specific amount of hydrazine derivatives containing at least two hydrazine residues as essential ingredients.

Claims

1. Fluorine-containing copolymer aqueous dispersion compositions crosslinkable at ambient temperature, comprise (A) fluorine-containing copolymer aqueous dispersions which can be obtained by the emulsion polymerization of 20-99 parts by weight of a mixture of (b) an acrylic acid alkyl ester with a C_{1-18} alkyl group and/or (c) a methacrylic acid alkyl ester with a C_{1-18} alkyl group, and (d) a copolymerizable ethylenically unsaturated monomer, in an aqueous medium in the presence of (a) 100 parts by weight of fluorine-containing polymer particles; the average particle size of the copolymer particles obtained from the emulsion polymerization is 0.05-3 μm , the amount of the ethylenically unsaturated monomer containing an active carbonyl group in the monomer mixture is 0.1-20 wt% and (B) hydrazine derivatives containing at least two hydrazine residues as essential ingredients; the amount of the hydrazine derivative is such that there is a 0.02-1 molar equivalent of hydrazine residue with respect to the active carbonyl group.

2. In the composition according to Claim 1, the fluorine-containing polymer is a vinylidene fluoride polymer.

3. In the composition according to Claim 2, the polymer is obtained by the polymerization of a monomer mixture of 70-95 mol% of vinylidene fluoride and 30-5 mol% of chlorotrifluoroethylene.

4. In any composition in Claims 1-3, the active carbonyl group-containing ethylenically unsaturated monomer is acetoacetoxyethyl methacrylate.

5. Aqueous coating materials, containing the composition of any of Claims 1-4.

6. Aqueous coating materials according to any of Claims 1-4 which can be used for exterior coatings and/or interior coatings for buildings or structures.

7. Coated products obtained by coating substrates with the aqueous coating materials according to Claim 5 or 6.

Detailed description of the invention

[0001]

The present invention pertains to fluorine-containing copolymer aqueous dispersions which can provide coating films with excellent low-temperature film formability, external appearance, strength, stain resistance, boiling water resistance, solvent resistance, weather resistance, and adhesion to substrates, aqueous coating materials containing the fluorine-containing copolymer aqueous dispersions, and coated products thereof.

[0002]

More precisely, the present invention pertains to (A) fluorine-containing copolymer aqueous dispersion compositions which are characterized in that they contain (a) fluorine-containing copolymer aqueous dispersions which can be produced by the seed polymerization of a monomer mixture of a specific amount of an acrylic acid alkyl ester and/or methacrylic acid alkyl ester and a specific amount of an active carbonyl group containing ethylenically unsaturated monomer in the presence of fluoropolymer particles and (b) a specific amount of hydrazine

derivatives containing at least two hydrazine groups, (B) aqueous coating materials containing the fluorine-containing copolymer aqueous dispersion compositions, and (C) coated products thereof.

[0003]

Prior art

Fluorine-containing coating materials are used as weather-resistant coating materials for interior and exterior coatings for buildings and structures. Various techniques have been developed to obtain fluorine-containing coating materials. Many of the fluorine-containing coating materials are dispersed in organic solvents. The use of organic solvents have problems in safety and environmental preservation, therefore the use of aqueous coating materials is preferable. The following methods are known for manufacturing fluorine-containing copolymer aqueous dispersion compositions.

[0004]

In Japanese Kokoku Patent No. Hei 4[1992]-55441 and Japanese Kokai Patent Application No. Hei 3[1991]-7784, it was disclosed that when ethylenically unsaturated monomers underwent emulsion polymerization in the presence of vinylidene fluoride copolymer particles in aqueous media, good film formability and film transparency were obtained which could not be obtained by emulsion blending. For the ethylenically unsaturated monomers, (meth)acrylic acid esters with C_{1-18} alkyl groups were illustrated. However, in the patents there is no description of

active carbonyl group-containing monomers which impart special functions to the fluorine-containing copolymer aqueous dispersion compositions. Moreover, the aqueous dispersion compositions prepared using the manufacturing methods do not have stain resistance, boiling water resistance, and solvent resistance, which are the objectives of the present invention.

[0005]

In Japanese Kokai Patent Application No. Hei 6[1994]-41490, fluorine-containing polymer aqueous coating material compositions containing (a) an aqueous dispersion obtained by the copolymerization of fluoroolefin and (b) an active carbonyl group-containing crotonaldehyde as essential components were disclosed, and it was suggested that the compositions could improve boiling water resistance and solvent resistance. However, the patent did not describe the improvement of external appearance and adhesion of coating films. Moreover, the patent did not suggest the use of hydrazine derivatives and aqueous dispersions which were prepared by the polymerization of an alkyl ester including an active carbonyl group-containing monomer with fluorine-containing polymers.

[0006]

Aqueous coating compositions containing acrylic copolymers prepared using acetoacetyl group-containing monomers were illustrated in Japanese Kokai Patent Application No. Hei 7[1995]-102208. However, no improvement of weather resistance was described in the patent.

[0007]

Problems to be solved by the invention

The objective of the present invention is to provide fluorine-containing copolymer aqueous dispersion compositions which can provide coating films with excellent low-temperature film formability, external appearance, strength, stain resistance, boiling water resistance, solvent resistance, weather resistance, and adhesion to substrates, aqueous coating materials containing the fluorine-containing copolymer aqueous dispersion compositions, and coated products thereof.

[0008]

The present inventors found that fluorine-containing copolymer aqueous dispersion compositions could attain the objective of the present invention, thereby they completed the present invention; the fluorine-containing copolymer aqueous dispersion compositions are composed of (A) a fluorine-containing copolymer aqueous dispersion which is a molecular-level mixture obtained by the seed polymerization of a specific amount of a monomer mixture of (b) an acrylic acid alkyl ester and/or (c) a methacrylic acid alkyl ester, and (d) an ethylenically unsaturated monomer, especially an ethylenically unsaturated monomer containing a specific amount of active carbonyl groups, in the presence of (a) fluorine-containing polymer particles (hereinafter sometimes referred to as seed particles), especially vinylidene fluoride (VdF), above all an aqueous dispersion containing 70-95 mol% of VF and 5-30 mol% of

chlorotrifluoroethylene (CTFE) and (B) hydrazine derivatives containing at least two hydrazine residues as essential components; the amount of the hydrazine derivative is such that there is a 0.02-1 molar equivalent hydrazine residue based on the active carbonyl groups.

[0009]

Means to solve the problems

The present invention pertains to fluorine-containing copolymer aqueous dispersions crosslinkable at room temperature comprising the following (A) and (B) as two essential components wherein (A) is a fluorine-containing copolymer aqueous dispersion which can be obtained by the emulsion polymerization of 20-99 parts by weight of a mixture of (b) an acrylic acid alkyl ester with a C₁₋₁₈ alkyl group and/or (c) a methacrylic acid alkyl ester with a C₁₋₁₈ alkyl group, and (d) a copolymerizable ethylenically unsaturated monomer, in an aqueous medium in the presence of (a) 100 parts by weight of fluorine-containing polymer particles; the average particle size of the copolymer obtained from the emulsion polymerization is 0.05-3 μm , the amount of the ethylenically unsaturated monomer containing an active carbonyl group in the monomer mixture is 0.1-20 wt%, and (B) is a hydrazine derivative containing at least two hydrazine residues; the amount of the hydrazine derivative is such that there is a 0.02-1 molar equivalent hydrazine residue with respect to the active carbonyl group.

[0010]

Examples of the active carbonyl group include acetoacetyl group, aldehyde group, etc. From the viewpoint of stability in aqueous media, acetoacetyl group is preferable.

[0011]

The present invention also pertains to aqueous coating materials containing the fluorine-containing copolymer aqueous dispersion compositions.

[0012]

The present invention also pertains to materials coated with the aqueous coating materials.

[0013]

Application modes of the invention

Examples of the fluorine-containing polymer that can be used as seed particles include homopolymers or copolymers such as chlorotrifluoroethylene (CTFE), tetrafluoroethylene (TFE), hexafluoropropylene (HFP), vinylidene fluoride (VF), trifluoroethylene (TrFE), vinyl fluoride (VF), etc., or copolymers formed from vinyl ethers such as an ethylenically unsaturated monomer, e.g., cyclohexyl vinyl ether (CHVE), ethyl vinyl ether (EVE), etc., which can copolymerize with the aforementioned monomers. Among these polymers, from the point of

view of compatibility, CTFE vinyl ether copolymers, VdF copolymers, etc., are preferable. Above all, Vd copolymers are preferable. In this case, copolymers with 70-95 mol% of VdF and 5-30 mol% of CTFE, preferably 75-90 mol% of VdF and 10-25 mol% of CTFE, more preferably 75-85 mol% of VdF and 15-25 mol% of CTFE can be used.

[0014]

In the above-mentioned fluorine-containing polymers when the VdF is 70 mol% or greater, the compatibility of seed particles and a monomer mixture of an acrylic acid alkyl ester and/or methacrylic acid alkyl ester and an ethylenically unsaturated monomer becomes good and excellent characteristics which are brought about by the compatibility can be obtained such as transparency and pencil strength of coating films (hereinafter sometimes referred to as "cast film") which were formed by drying emulsion-like fluorine-containing aqueous dispersion compositions. When the CTFE is less than 5 mol%, sometimes the solubility of the seed particles in a monomer mixture of an acrylic acid alkyl ester and/or methacrylic acid alkyl ester and an ethylenically unsaturated monomer is reduced, and sometimes the swelling of the monomer mixture to the seed particles cannot be carried out rapidly during seed polymerization, the transparency of the cast films obtained from the thus-obtained fluorine-containing copolymer compositions is reduced, and when coating films are prepared from the coating materials, gloss and adhesion cannot be obtained.

[0015]

The amount of ethylenically unsaturated monomer which can copolymerize with the above-mentioned VdF and CTFE monomers is 0-30 mol%, preferably 10-25 mol%, more preferably 10-20 mol%.

[0016]

When seed particles are selected from the group consisting of CTFE, VdF, and TFE or VF, the seed particles become more soluble in the monomer mixture and during seed polymerization the swelling of the monomer mixture to the seed particles can be carried out rapidly, and the cast films prepared from the thus-obtained fluorine-containing copolymer compositions become more transparent and glossy films can be prepared from the coating materials.

[0017]

When the seed particles are composed of CTFE, VdF, and HFP or TrFE, the seed particles are dissolved easily in the monomer mixture, and the compatibility of HFP and TrFE with acrylic and/or-methacrylic copolymer is improved, the cast films obtained from the thus-obtained fluorine-containing copolymer compositions become more transparent and highly glossy coating films can be obtained.

[0018]

The average particle size of the fluorine-containing polymers in the present invention is closely related to the average particle size of the fluorine-containing polymers after seed polymerization. In order to obtain fluorine-containing polymers with an average particle size of 0.05-3 μm , preferably 0.05-0.5 μm , more preferably 0.1-0.2 μm after the seed polymerization, it is desirable for the average particle size of the fluorine-containing polymers to be 0.05-2.8 μm , preferably 0.05-0.48 μm , more preferably 0.09-0.18 μm .

[0019]

In the present invention, the synthesis of seed particles (a) usually can be carried out by emulsion polymerization in aqueous dispersions. At this time the concentration of the seed particles in the aqueous dispersion after synthesis is preferably 35 wt% or greater, more preferably 40 wt% or greater. The concentration of the seed particles is closely related to the concentration of copolymers in the fluorine-containing copolymer aqueous dispersion (A) after seed polymerization. It is necessary for the concentration of the copolymer after seed polymerization to be usually 45-50 wt%. If it is less than that concentration, the adjustment of viscosity during the preparation of a coating material is so difficult that it is not practical.

[0020]

In case the concentration of the copolymer in the fluorine-containing copolymer aqueous dispersion (A) is less than 45 wt%, the concentration can be increased by concentrating, however in this case because the formation of secondary particles causes the fluorine-containing copolymer in the aqueous dispersion to become unstable, which is disadvantageous to the external appearance and the stability of preservation, it is therefore preferable to obtain the fluorine-containing copolymer aqueous dispersion without using a concentration process. From this point of view it is preferable for the concentration of the aqueous dispersion after seed particle synthesis to be 35 wt% or greater, more preferably 40 wt% or greater.

[0021]

The fluorine-containing copolymer which can be used as seed particles can be obtained by a common emulsion polymerization as mentioned above.

[0022]

For example, it can be prepared by the emulsion polymerization of a monomer mixture containing fluoroolefin in the presence of 0.01-1.0 wt% (based on water) of a fluorine-containing reactive emulsifier having a hydrophilic site and 0.1-1.0 wt% of a fluorine-containing emulsifier.

[0023]

It can also be prepared by the emulsion polymerization of a monomer mixture containing fluoroolefin in the presence of 1.0 wt% or less (based on water), preferably 0.5 wt% or less, more preferably 0.2 wt% (lower limit is usually 0.01 wt%) of a fluorine-containing surfactant and 0.001-0.1 wt% based on water), preferably 0.01-0.05 wt% of a nonionic surfactant containing no fluorine.

[0024]

The aqueous dispersion which was obtained by using these methods can stably contain 30-50 wt% of seed particles with an average particle size 0.2 μm or less.

[0025]

Examples of a fluorine-containing reactive emulsifier having a hydrophilic site include $\text{CF}_2=\text{CF}-(\text{CF}_2\text{CFX})_n\text{Y}$ (wherein X is F or CF_3 , Y is SO_3M , COOM (M is a hydrogen atom, amine, ammonium, or alkali metal atom), n is an integer), $\text{CF}_2=\text{CF}-\text{O}(\text{CFX})_n\text{Y}$ (wherein X, Y, and n are the same as those mentioned above), $\text{CH}_2=\text{CF}-\text{CF}_2-\text{O}(\text{CF}(\text{CF}_3)\text{CF}_2\text{O})_n-\text{CF}(\text{CF}_3)\text{Y}$ (wherein Y and n are the same as those mentioned above), $\text{CF}_2=\text{CF}-\text{CF}_2-\text{O}(\text{CF}(\text{CF}_3)\text{CF}_2\text{O})-\text{CF}(\text{CF}_3)\text{Y}$ (wherein Y and n are the same as those mentioned above). From the point of view of solubility in water and surface activity, it is preferable for n to be 0-3.

[0026]

More specifically, $\text{CH}_2=\text{CF}-\text{CF}_2-\text{O}((\text{CF}_3)\text{CFCF}_2\text{O})_n-(\text{CF}_3)\text{CFCOOH}$ with $n = 0-2$ can be used.

[0027]

The polymerization temperature is 20-120°C, preferably 30-70°C. When the polymerization temperature is lower than 20°C, generally speaking, the latex formed is less stable, while when the polymerization temperature is higher than 120°C, there is a tendency for the polymerization rate to stall by chain reaction. Depending on the type of polymer, polymerization is usually carried out under a pressure of 1.0-50 kgf/cm² (gauge pressure) and heating for 5-100 h.

[0028]

For the fluorine-containing emulsifier used in the emulsion polymerization of seed particles, one or a mixture of at least two fluorine-containing compounds having fluorine atoms and surface activity can be used. For example, the acid which can be represented by $\text{X}(\text{CF}_2)_n\text{COOH}$ (n is 6-20 (integer), X is F or H) and its alkali salt, ammonium salt, amine salt, or quaternary ammonium salt; the acid which can be represented by $\text{Y}(\text{CH}_2\text{CF}_2)_m\text{COOH}$ (m is 6-13 (integer), Y is F or Cl), its alkali salt, ammonium salt, amine salt, or quaternary ammonium salt can be used. More specifically, ammonium perfluorooctanoate, ammonium perfluorononanoate, etc., can be used. In addition, known fluorine-containing surfactants can also be used.

[0029]

In emulsion polymerization for obtaining seed particles, a small amount of nonionic surfactant containing no fluorine can also be used in the presence of a fluorine-containing surfactant. For example, polyoxyethylene alkyl ethers, polyoxyethylene alkylphenyl ethers, polyoxyethylene alkyl esters, sorbitan alkyl esters, polyoxyethylene sorbitan alkyl esters, glycerin esters and their derivatives. More specific examples of polyoxyethylene alkyl ethers include polyoxyethylene lauryl ether, polyoxyethylene cetyl ether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene behenyl ether, etc.; examples of polyoxyethylene alkylphenyl ether include polyoxyethylene nonylphenyl ether, polyoxyethylene octylphenyl ether, etc.; examples of polyoxyethylene alkyl ester include polyethylene glycol monolaurate, polyethylene glycol monooleate, polyethylene glycol monostearate, etc.; examples of sorbitan alkyl ester include polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan monopalmitate polyoxyethylene sorbitan monostearate, polyoxyethylene sorbitan monooleate, etc.; examples of polyoxyethylene sorbitan alkyl ester include polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan monopalmitate, polyoxyethylene sorbitan monostearate, etc.; examples of glycerin ester include glyceryl monomyristate, glyceryl monostearate, glyceryl monooleate, etc. Examples of their derivatives include polyoxyethylene alkylamine, polyoxyethylene alkylphenyl ether for aldehyde condensation product, polyoxyethylene alkyl ether phosphate salt, etc. Especially preferable are polyoxyethylene alkyl ethers and polyoxyethylene alkyl esters and the HLB value is 10-18. Specific examples include polyoxyethylene lauryl ether

(EO: 5-20, EO is the number of ethylene oxide units), polyoxyethylene glycol monostearate EO: 10-55), polyoxyethylene glycol monooleate (EO: 6-10).

[0030]

In the present invention, a monomer mixture containing an acrylic acid ester and/or methacrylic acid ester and an ethylenically unsaturated monomer undergoes seed polymerization in the presence of seed particles.

[0031]

In the present invention, examples of the acrylic acid ester with a C_{1-18} alkyl group include methyl acrylate, ethyl acrylate, propyl acrylate, n-butyl acrylate, isobutyl acrylate, n-amyl acrylate, isoamyl acrylate, n-hexyl acrylate, 2-ethylhexyl acrylate, lauryl acrylate, etc. Among them, acrylic acid esters with C_{1-3} alkyl groups are preferable, especially acrylic acid esters with C_{1-2} alkyl groups are preferable. A single or a mixture of at least two of the acrylic acid esters can be used.

[0032]

Examples of the methacrylic acid ester with a C_{1-18} alkyl group include methyl methacrylate, ethyl methacrylate, propyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, n-amyl methacrylate, isoamyl methacrylate, n-hexyl methacrylate, 2-ethylhexyl methacrylate, lauryl methacrylate, etc. Among them methacrylic acid esters with C_{1-3} alkyl groups are preferable,

especially methacrylic acid esters with C_{1-2} alkyl groups are preferable. The methacrylic acid esters can be used alone or as a mixture.

[0033]

In the present invention, in case an acrylic acid alkyl ester and methacrylic acid alkyl ester are used together, there is no limitation on the ratio between them and the ratio can be selected suitably depending on the desired characteristics of the aqueous dispersion of the polymer particles.

[0034]

Vinyl compounds can be the ethylenically unsaturated monomers which can copolymerize with the acrylic acid alkyl ester and/or methacrylic acid alkyl ester, and it is important for highly active carbonyl group containing ethylenically unsaturated monomers to be essential monomers.

[0035]

Examples of vinyl compounds in the present invention include amides such as acrylamide, methacrylamide, N-methylacrylamide, N-methyl methacrylamide, N-methylolacrylamide, N-methylol methacrylamide, N-alkylacrylamide, N-alkyl methacrylamide, N,N-dialkylacrylamide, N,N-dialkyl methacrylamide, etc.; acrylic acid esters such as 2-hydroxyethyl acrylate, N,N-dialkylaminoethyl acrylate, glycidyl acrylate, fluoroalkyl acrylate, etc.; methacrylic acid esters such as 2-hydroxyethyl

methacrylate, N,N-dialkylaminoethyl methacrylate, glycidyl methacrylate (GMA), fluoroalkyl methacrylate, cyclohexyl methacrylate, ethylene glycol dimethacrylate, etc.; vinyl ethers such as allyl glycidyl ether, etc.; conjugated dienes such as 1,3-butadiene, isoprene, chloroprene, etc.; aromatic vinyl compounds such as styrene, α -methylstyrene, halogenated styrene, divinylbenzene etc.; vinyl cyanides such as acrylonitrile, methacrylonitrile, etc. These monomers can be used alone or as a mixture. Vinyl esters such as vinyl acetate, Veava 9 and Veova 10 (Shell-Kagaku K.K.) which are vinyl ester mixtures of branched-chain alkyls can also be used.

[0036]

Examples of active carbonyl group-containing ethylenically unsaturated monomer include acetoacetoxyethyl methacrylate, acetoacetoxyethyl acrylate, vinyl acetoacetate, vinyl γ,γ -dimethyl-6-ketocarboxylate, acrolein, methacrolein, crotonaldehyde, cinnamic aldehyde, etc. However, from the viewpoint of weather resistance and toxicity during polymerization, the use of acetoacetoxyethyl methacrylate is preferable.

[0037]

The amount of the active carbonyl group-containing ethylenically unsaturated monomer to be used is 0.1-20 wt%, preferably 1-10 wt% based on the mixture of the acrylic acid alkyl ester and/or methacrylic acid alkyl ester and the ethylenically unsaturated monomer. When the amount of the active

carbonyl group-containing ethylenically unsaturated monomer used is less than 0.1 wt%, the stain resistance such as carbon staining of the coating material composition, boiling water resistance, solvent resistance, and adhesion to substrates which are the objectives of the present invention cannot be improved, while when it is greater than 20 wt% there is a tendency for the compatibility of the seed particles to become poor, and the gloss and weather resistance of the coating films are reduced.

[0038]

The total amount of the ethylenically unsaturated monomer and acrylic acid alkyl ester and/or methacrylic acid alkyl ester is 20-99 parts, preferably 30-99 parts, more preferably 40-99 parts based on 100 parts (parts by weight, hereinafter the same) of seed particles. When it is less than 20 parts, the transparency, gloss, and adhesion (to substrates) of coating films formed tend to be reduced, while when it is greater than 99 parts, the weather resistance tends to be reduced.

[0039]

The seed polymerization of the ethylenically unsaturated monomer and acrylic acid alkyl ester and/or methacrylic acid alkyl ester can be carried out under the same conditions as those of common emulsion polymerization. For example, surfactants, polymerization initiators, chain-transfer agents, if necessary chelating agents, pH-adjusting agents, and solvents can be added to the aqueous media and then the reaction is carried out at 20-90°C, preferably 20-80°C, more preferably 30-70°C for 0.5-6 h.

[0040]

In seed polymerization, any of the following three methods can be used, i.e., either the whole amount of the monomers can be added at once to the reaction system in the presence of seed particles or a portion of the monomers is added and then the rest of the monomers is continuously added or added stepwise or all of the monomers are added continuously.

[0041]

When seed polymerization of the ethylenically unsaturated monomer and acrylic acid alkyl ester and/or methacrylic acid alkyl ester is carried out in the presence of seed particles, first of all, swelling of the seed particles is caused by the ethylenically unsaturated monomer and acrylic acid alkyl ester and/or methacrylic acid alkyl ester and then the ethylenically unsaturated monomer and acrylic acid alkyl ester and/or methacrylic acid alkyl ester are dissolved in the seed particles, and by the addition of a polymerization initiator, the ethylenically unsaturated monomer and acrylic acid alkyl ester and/or methacrylic acid alkyl ester are polymerized, followed by the formation of copolymer particles wherein the molecular chains of the polymers of the ethylenically unsaturated monomer and acrylic acid alkyl ester and/or methacrylic acid alkyl ester are crosslinked with the molecular chains of the fluorine-containing polymers. When the ethylenically unsaturated monomer and acrylic acid alkyl ester and/or methacrylic acid alkyl ester are copolymerized with multifunctional monomers a semi-interpenetrating structure (S-IPN) can also be formed. Examples

of the multifunctional monomer include monoglycol dimethacrylate, diglycol dimethacrylate, etc.

[0042]

For the surfactants which can be used in seed polymerization, anionic surfactants, nonionic surfactants or a combination thereof can be used and amphoteric surfactants also can be used. Examples of the anionic surfactant which can be used include higher alcohol sulfate salt esters such as sodium alkyl sulfonate, sodium alkylbenzene sulfonate, dialkyl sulfosuccinate sodium salt, alkylbiphenyl ether disulfonic acid sodium salt, etc. Examples of nonionic surfactant which can be used include polyoxyethylene alkyl ethers, polyoxyethylene alkylphenyl ethers, polyoxyethylene alkyl esters, polyoxyethylene alkylphenyl esters, sorbitan alkyl esters, glycerin esters, and their derivatives. Examples of amphoteric surfactants which can be used include lauryl betaines, etc. The so-called reactive emulsifiers which can copolymerize with the acrylic acid ester, methacrylic acid ester, and ethylenically unsaturated monomer, for example, sodium styrene sulfonate, sodium alkyl sulfosuccinate, etc., can be used. The amount of surfactant which can be used is usually 0.05-0.5 part based on 100 parts of the sum of the acrylic alkyl ester and/or methacrylic acid alkyl ester and ethylenically unsaturated monomer.

[0043]

There is no limitation on the polymerization initiators as long as they can generate free radicals at 20-90°C which can be

used for free radical reaction in aqueous media. In some cases it can be combined with a reducing agent and then used. Examples of water-soluble polymerization initiator include persulfate and hydrogen peroxide; examples for the reducing agent include sodium pyrobisulfite, sodium bisulfite, sodium L-ascorbate, etc. Examples of an oil-soluble polymerization initiator include diisopropyl peroxydicarbonate (IPP), benzoyl peroxide, dibutyl peroxide, azobisisobutyronitrile (AlBN), etc. The amount of polymerization initiator to be used is usually 0.05-2.0 parts based on 100 parts of the sum of other acrylic alkyl ester and/or methacrylic acid alkyl ester and ethylenically unsaturated monomer.

[0044]

The polymerization temperature is 20-90°C, preferably 30-70°C.

[0045]

Examples of chain-transfer agents which can be used include halogenated hydrocarbons (such as chloroform, carbon tetrachloride, etc.), mercaptans (such as n-dodecyl mercaptan, tert-dodecyl mercaptan, n-octyl mercaptan, isooctyl thioglycolate, etc.). Above all, isooctyl thioglycolate and n-dodecyl mercaptan are preferable from the point of view of chain-transfer effect and odor. The amount of chain-transfer agent to be used is usually 0-0.5 part based on 100 parts of the sum of the acrylic alkyl ester and/or methacrylic acid alkyl ester and ethylenically unsaturated monomer.

[0046]

For the solvent, a small amount of methyl ethyl ketone, acetone, trichlorotrifluoroethane, methyl isobutyl ketone, ethyl acetate, etc. can be used as long as that amount does not adversely affect the operability, prevention of disasters, environmental safety, and manufacturing safety. Sometimes by the addition of solvents, the swellability of monomers to seed particles can be improved.

[0047]

Fluorine-containing copolymer aqueous dispersions of the present invention can be obtained as mentioned above; however, from the point of view of the improvement of film formability and adhesion to substrates which are the objective of the present invention, it is preferable to carry out seed polymerization of methacrylic acid alkyl ester and copolymerizable monomers in an aqueous dispersion containing fluorine-containing polymer particles having a T_g between -35°C and 25°C , thereby the minimum film-forming temperature of the fluorine-containing copolymer aqueous dispersion can be arbitrarily set by the seed particles at any temperature between 0°C and 70°C by the selection of the T_g .

[0048]

The effect of methacrylic acid alkyl esters with a C_{1-6} side chain on the reduction of weather resistance is small, therefore they are preferable; however, with a decrease in the carbon

number of side chain, the compatibility with the VdF copolymer can be increased, therefore methacrylic acid alkyl esters with a C_{1-3} side chain are more preferable, and methacrylic acid alkyl esters with a C_1 side chain (one-carbon atom side chain)- is most preferable.

[0049]

For further improvements in solvent resistance and water resistance, multifunctional monomers such as ethylene glycol dimethacrylate, propylene glycol dimethacrylate, etc., can be copolymerized.

[0050]

When emulsion polymerization is carried out under the condition in which monomers are homogeneously dissolved in seed particles, hydrophilic site-containing compounds which can be contained in low molecular weight polymers or oligomers can be used also as the copolymerizable ethylenically unsaturated monomers. The hydrophilic site means a site with a hydrophilic group or hydrophilic bond. The hydrophilic group can be anionic, nonionic, amphoteric, and a combination thereof, however, nonionic and anionic hydrophilic groups are preferable. Known reactive emulsifiers are also included in them.

[0051]

For the above-mentioned monomers, examples of commercially available reactive emulsifier include Blemmer PE-350, Blemmer

PME-400, Blemmer 70 PEP 350 B, Uniox PKA 5002, Uniox PKA 5003, Uniox PKA 5004, Nippon Oils & Fats Co., Ltd.), NK Ester M-40G, NK Ester M-90G, NK Ester M-230G, NK Ester AMP-600, NK Ester CB-1, NK Ester SA, NK Ester A-SA (Shinnakamura Kagaku K.K.), Eleminol JS2, Eleminol RS30 (Sanyo Chemical Industries, Ltd.), RMA 150M, RMA 300M, RMA 450M (Nippon Nyukazai Co., Ltd.), etc.

[0052]

Among the above-mentioned monomers, allyl ether derivatives which do not exert adverse effects on weather resistance are preferable.

[0053]

The average particle size of fluorine-containing copolymers in aqueous dispersions obtained by seed polymerization in the present invention is preferably 0.05-3 μm , more preferably 0.05-0.5 μm , most preferably 0.1-0.2 μm . When the average granule size is less than 0.05 μm , the viscosity of the aqueous dispersion increases, therefore a high-temperature aqueous dispersion cannot be obtained. When the average granule size of the fluorine-containing copolymer is greater than 3 μm , particles precipitate and furthermore coagulate during the storage of the aqueous dispersion. When coating films are prepared, films with no gloss are obtained.

[0054]

By using the above-mentioned procedure, fluorine-containing copolymer aqueous dispersions can be obtained. By adding a hydrazine derivative with at least two hydrazine residues as an essential component to the fluorine-containing copolymer aqueous dispersion in such a way that there is a 0.02-1 molar equivalent of hydrazine residue based on the active carbonyl group, fluorine-containing copolymer aqueous dispersion compositions crosslinkable at ambient temperature can be obtained.

[0055]

The above-mentioned amount of the hydrazine derivative to be added is such that there is a 0.02-1 molar equivalent, preferably 0.05-0.5 molar equivalent of hydrazine residue based on the carbonyl group in the copolymer.

[0056]

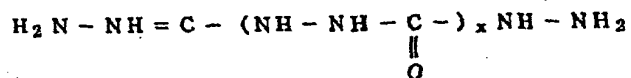
If the amount of the hydrazine derivative is less than 0.02 mol%, the crosslinking density of the cast films is so low that the objective of the present invention cannot be attained, while if it is greater than 1 mol% free hydrazine can form from the hydrazine derivative by hydrolysis; the toxicity of the hydrazine thus formed is a problem and the gloss of the coating films is reduced by the unreacted hydrazine derivative.

[0057]

The above-mentioned hydrazine derivative contains at least two hydrazine residues and those derived from saturated aliphatic dicarboxylic acids are particularly advantageous. Especially important is aliphatic dicarboxylic acid dihydrazides with 2-10 carbon atoms. Examples of these suitable dihydrazides include malonic acid dihydrazide, succinic acid dihydrazide, glutaric acid dihydrazide, adipic acid dihydrazide and/or sebacic acid dihydrazide. Carbonic acid polyhydrazides such as carbonic acid dihydrazide, compounds which can be represented by the general formula

[0058]

[Structure 1]

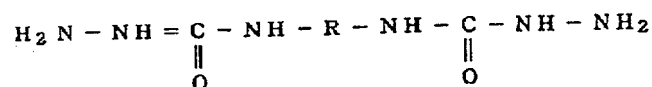


[0059]

(wherein x is 1-5, preferably 1-3 (integer), and bissemicarbazide, especially aliphatic, alicyclic, or aromatic bissemicarbazide which can be represented by the general formula

[0060]

[Structure 2]



[0061]

(wherein R is straight-chain or branched-chain aliphatic residue with 2-7 carbon atoms or straight-chain or branched-chain cyclic carbon residue with 6-8 carbon atoms such as an o-, m-, or p-phenylene group, toluylene group, cyclohexylidene group, or methylcyclohexylidene group) are also very suitable. Examples of hydrazide derivatives which can be suitably used include aromatic polycarboxylic acid polyhydrazide, poly(acrylic acid) polyhydrazide containing at least two and can contain as many as 20-100 hydrazide groups in one molecule, trihydrazide, and tetrahydrazide. Examples of the aromatic polycarboxylic acid polyhydrazide include phthalic acid dihydrazide such as terephthalic acid or isophthalic acid, or pyromellitic acid dihydrazide, trihydrazide or tetrahydrazide.

[0062]

Examples of the trihydrazide include nitrotriacetic acid hydrazide, etc. And examples of the tetrahydrazide include ethylenediaminetetraacetic acid tetrahydrazide, etc.

[0063]

Examples of other usable hydrazine derivatives include di- or trihydrazine triazine, thiocarbohydrazide, N,N-diaminoguanidine, hydrazine-pyridine derivative, bithiosemicarbazide, alkylene bisacrylamide, dihydrazine alkane, aromatic hydrocarbon dihydrazide or monoolefinically unsaturated dicarboxylic acid dihydrazide.

[0064]

Examples of the above-mentioned hydrazine-pyridine derivative include 2-hydrazinopyridine-5-carboxylic acid hydrazide, 3-chloro-2-hydrazinopyridine-5-carboxylic acid hydrazide, 6-chloro-2-hydrazinopyridine-4-carboxylic acid hydrazide or 2,5-dihydrazinopyridine-4-carboxylic acid hydrazide, etc. Examples of the above-mentioned aromatic hydrocarbon dihydrazide include 1,4-dihydrazinobenzol, 1,3-dihydrazinobenzol or 2,3-hydrazinonaphthalene, etc. Examples of the above-mentioned monoolefinically unsaturated dicarboxylic acid dihydrazide include maleic acid dihydrazide, fumaric acid dihydrazide or itaconic acid dihydrazide, etc.

[0065]

0.0002-0.02 mol% of heavy metal ions (in the form of heavy metal salt) (based on 1 mole of hydrazine derivative) can be added to a mixture of an aqueous dispersion of active carbonyl group-containing fluorine-containing copolymer particles and a hydrazine derivative containing at least two hydrazine residues,

to prevent the formation of the amount of free hydrazine which disturbs the mixture during the storage of the mixture and to promote crosslinking. Examples of the heavy metal salt include water-soluble heavy metal salts, especially chlorides and sulfates, acetates are excellent, and water-soluble salts of copper, zinc, iron, chromium, manganese, lead, vanadium, cobalt and/or nickel are preferable, and above all, water-soluble salts of copper, iron, manganese, vanadium and/or cobalt are more preferable. Examples of the water-soluble salt include cupric chloride, cupric sulfate, zinc sulfate, ferrous chloride, cobalt (II) chloride, manganese (II) chloride, lead (II) sulfate, nickel (II) chloride, chromium nitrate, vanadium acetate and chromium (II) sulfate.

[0066]

When manufacturing an aqueous dispersion containing active carbonyl group-containing fluorine-containing copolymer particles, the hydrazine derivative and heavy metal ions or its salt, the heavy metal salt is preferably prepared in advance in the form of an aqueous solution and generally speaking it is added after polymerization and in many cases it is added with the hydrazine derivative or it is added after the addition of the hydrazine derivative.

[0067]

For the fluorine-containing copolymer aqueous dispersion compositions of the present invention, from the point of view of obtaining good boiling water resistance, solvent resistance,

weather resistance, and gloss, it is preferable for the fluorine-containing copolymer to be a vinylidene polymer, the methacrylic acid alkyl ester to be methyl methacrylate, the active carbonyl group-containing ethylenically unsaturated monomer to be acetoacetoxyethyl methacrylate, and the hydrazine derivative to be adipic acid dihydrazide.

[0068]

As aqueous coating materials, the fluorine-containing polymer aqueous dispersion compositions of the present invention can be used as coatings for the surface protection of concrete and coating materials for coating paper by blending with additives such as pigments, thickeners, dispersion agents, antifoaming agents, antifreeze agents, film-forming aids, etc., which are generally used in aqueous emulsion coating materials.

[0069]

The fluorine-containing polymer aqueous dispersion compositions of the present invention can be used as exterior and/or interior aqueous coating materials for buildings or structures.

[0070]

Conventionally known methods can be used for coating the aqueous coating material of the present invention. For coating, a conventionally known coating apparatus such as a brush, roller,

roll coater, air spray, airless spray, electrostatic coater, dipping coater, electrodeposition coater, etc., can be used.

[0071]

The aqueous coating materials of the present invention can be used in the coating of not only metals such as iron, aluminum, copper, or alloys thereof, but also inorganic materials such as glass, cement, concrete, etc., resins such as FRP, acrylic resin, vinyl chloride resin, polycarbonate, polyurethane, etc., and other substrates such as wood, fibers, etc. If necessary, substrates can be subjected to pretreatment and surface treatment, and then coated with coating material compositions of the present invention after a suitable undercoating or precoating. Depending on the types of hardening agent, after coating, the coating films are usually hardened by drying at 5-300°C for 30 sec to one week. There is no limitation on the thickness of the coating films, however, it is usually 1-200 μm , preferably 5-100 μm , more preferably 10-50 μm thick.

[0072]

The thus-obtained coated products are excellent in adhesion, weather resistance, and chemical resistance and the surface of the coating films has lubricity, therefore they can be used in broad fields. Namely they can be used for interior and exterior coating of electric appliances (electric ranges, toasters, refrigerators, washing machines, hair dryers, television sets, video players, amplifiers, radios, electric pots, rice cookers, radio cassettes, cassette decks, compact disk players, video

cameras, etc.); for interior and exterior coating of indoor and outdoor air conditioners, nozzles and ducts, air cleaners, heaters; for coating fluorescent lamps, chandeliers, reflecting plates, furniture, machine parts, ornaments, combs, eye-glass frames, natural fibers, synthetic fibers (yarns and fabrics thereof), office machines (telephones, facsimiles, copiers (including rollers)), cameras, overhead projectors, prototype projectors, watches, slide projectors, desks, bookcases, lockers, document shelves, chairs, bookends, electronic writing boards, etc.); for coating automobiles (wheels, door mirrors, chenille fabric, door knobs, number plates, handles, instrumental panels, etc.) or kitchen utensils (range hoods, sinks, kitchen tables, kitchen knives, chopping boards, faucets of waterworks, gas ranges, ventilation fans, etc.); for indoor coating of room dividers, bus units, shutters, blinds, curtain rails, accordion curtains, walls, floors, etc.; for house exterior coating of outer walls, handrails, doors) shutters etc., for exterior coating of buildings; for exterior coating of sizing materials for kilns, foamed concrete panels, concrete panels, curtain walls; for exterior coating of building materials such as vinyl acetate and steel plates and sheets, etc.; and for coating window glass and others uses.

[0073]

Application examples

Next, application examples will be used to better explain the present invention, however, the present invention is not limited to these application examples.

[0074]

Synthesis Example 1

(synthesis example of seed particles, the same for the following synthesis examples)

500 mL of deionized water, 0.5 g of ammonium perfluorooctanoate, and 0.5 g of reactive emulsifier which can be represented by the formula $\text{CH}_2=\text{CF}-\text{CF}_2-\text{OCF}(\text{CF}_3)\text{CF}_2\text{O}-\text{CF}(\text{CF}_3)\text{COOH}$ were put in a 1 L-capacity pressure-resistant reactor equipped with an agitator. After the air in the reactor was replaced by nitrogen to remove the air in the reactor, a monomer mixture of VdF/TFE/CTFE with 74/14/12 mol% ratios was put in the reactor at a pressure of 8 kgf/cm² at 60°C. Then, 1.5 g of ethyl acetate and 0.2 g of ammonium persulfate were put in the reactor and the monomer mixture was added continuously to the reactor in such a way that the pressure inside the reactor was 8 kgf/cm² and then the reaction was carried out for 45 h, followed by restoring the interior of the reactor to ambient temperature and ambient pressure.

[0075]

The following items were measured for aqueous dispersion.

[0076)

Solid matters: An aqueous dispersion sample was dried in a vacuum drying oven at 150°C for 1 h, the weight after drying was

divided by the weight of the aqueous dispersion prior to drying and the thus-obtained value was multiplied by 100.

Average particle size: It was measured using an apparatus for particle size measurement by laser light scattering (ELS-3000, Otsuka Denshi Co.).

[0077]

The results are shown in Table I.

[0078]

Synthesis Examples 2-5

Aqueous dispersions of Synthesis Examples 2-5 were prepared using the same method which was used in Synthesis Example 1 except that the compositions of the monomer mixture were changed as shown in Table I and then the same measurements as those in Synthesis Example 1 were carried out. The results are shown in Table I.

[0079]

Synthesis Example 6

As shown in Table I, 20.0 g of cyclohexyl vinyl ether (CHVE), 11.4 g of ethyl vinyl ether (EVE), 4.5 g of hydrophilic site-containing macromonomer (PKAS 003, Nippon Oils & Fats Co., Ltd.), 66.1 g of deionized water, 0.35 g of ammonium perfluorooctanoate (emulsifier), 0.35 g of potassium carbonate

(K_2CO_3), 0.02 g of sodium bisulfite ($NaHSO_3$), and 0.08 g of ammonium persulfate (initiator) were put in a 200-mL stainless steel autoclave equipped with an agitator. Then the autoclave was cooled with ice and the air in the autoclave was replaced by nitrogen by adding nitrogen gas at 3.5 kgf/cm² pressure, followed by degassing. The removal of air by pressurization with nitrogen gas followed by degassing was repeated twice and then the autoclave was degassed until [a pressure of] 10 mm Hg [was obtained] to remove the oxygen dissolved, and then 38.0 g of chlorotrifluoroethylene (CTFE) was put in the autoclave and the reaction was carried out at 30°C for 12 h to give the aqueous dispersion of Synthesis Example 6 and then the same measurements as those carried out in Synthesis Example I were carried out. The results are shown in Table I.

[0080]

Table I

		① シード粒子の合成例					
		1	2	3	4	5	6
② 単量体 仕込量 (モル%)	VdF	74	78	65	68	97	
	TFE	14	16		20		
	CTFE	12			12	3	50
	HFP		6	45			
	CHVE						25
	EVE						25
③ 水性 分散液	④ 固形分濃度 (重量%)	40	40	35	35	30	50
	⑤ 平均粒子径 (μm)	0.12	0.13	0.10	0.13	0.14	0.18
	⑥ 反応時間 (hrs)	45	43	36	30	48	12

⑦ * 1 シード粒子をシード重合する前の水性分散液

Key: 1 Synthesis example for seed particles
2 Amount of monomers fed (mol%)
3 Aqueous dispersion
4 Concentration of solid matter (wt%)
5 Average particle size
6 Reaction time
7 * 1 Aqueous dispersion prior to seed polymerization of seed particles.

[0081]

Application Example 1

70 g of the aqueous dispersion obtained in Synthetic Example 1 was put in a 200 mL-capacity 4-necked flask equipped with an impeller, a condenser, and a thermometer. Then 0.5 wt% (based on the solid matter of the aqueous dispersion) of JS 2 (Sanyo Chemical Industries, Ltd.) was added and while it was agitated it was heated in a water bath. When the temperature reached 80°C, an emulsion prepared by emulsifying a mixture of 10 g of methyl methacrylate (hereinafter referred to as MMA), 1.2 g of acetoacetoxyethyl methacrylate (hereinafter referred to as AAEM), 1.5 g of RS 30 (Sanyo Chemical Industries, Ltd.), and 0.3 g of isooctyl thioglycolate with 0.5 wt% of JS 2 (Sanyo Chemical Industries, Ltd.) was added dropwise over a period of 1 h. Immediately after the addition, 1 mL of 2 wt% of an aqueous ammonium persulfate solution was added to start the reaction. 3 h after the start of the reaction, the temperature of the reactor was raised to 85°C and after maintaining the temperature for 1 h it was cooled, and after the pH was adjusted to 7 with aqueous ammonia, an amount of a 10% aqueous adipic acid dihydrazide

solution was added to the aqueous dispersion which was a 1.0 molar equivalent hydrazine residue with respect to the active carbonyl group of AAEM, followed by filtering through a 300-mesh screen to give a bluish-white fluorine-containing copolymer aqueous dispersion composition.

[0082]

The following tests were carried out for the aqueous dispersion composition.

[0083]

(I) Evaluation of characteristic of the aqueous dispersion composition

Concentration of solid matter and average particle size: they were measured using the same methods as mentioned above.

Minimum film-forming temperature (MET): The minimum temperature for continuously forming a film was measured using a thermal gradient tester (Rigaku Kogyo K.K.).

[0084]

(2) Evaluation of the characteristics of the coating films

To 100 parts of solid matter of the aqueous dispersion composition obtained in Application Example 1, 50 parts of titanium oxide (trade name: CR90, (Ishihara Sangyo Kaisha, Ltd.) as a filler, 2 parts of Nopcosperse [transliteration] SN 5027

(San Nopco Ltd.) as a dispersion agent, 1 part of ethylene glycol as an antifreeze agent, 0.5 part of FS antifoam 013 B (Nippon Nyukazai Co., Ltd.) as an antifoaming agent, 0.5 part of UH 420 (Asai Denka Kogyo K.K.) as a thickener, 10 parts of Texanol CS 12 (Chisso Corporation) as a film-forming aid, and 5 parts of butylcarbinol acetate were added, and then the mixture was thoroughly agitated with a Disper [transliteration] agitator to give a coating material.

[0085]

Low-temperature film formability: A slate coated with the thus-obtained coating material and aqueous acrylic sealer Movinyl 940 (Hoechst Gosei K. K.) was put in a thermostat at 5°C for 12 h, then it was stretched to a 40- μ m thick coating film using an applicator, dried in a thermostat at 5°C for 24 h, and then cracking during film formation was visually observed and evaluated based on the following criteria.

- A no cracking at all
- B some cracking
- C cracking over the entire coating film

[0086]

Gloss: A glass plate was coated with the thus-obtained coating material using an applicator so that a 20 μ m-thick film was obtained. After the film was dried at room temperature for 4 weeks, the gloss at a reflection angle of 60° was measured using a glossmeter (Suga Shikenki K.K.).

[0087]

Pencil hardness: The hardness of the coating film on the glass plate was measured using the pencil hardness test method described in JIS K 5400.

[0088]

Adhesion: A slate which had been coated with aqueous acrylic scaler Movinyl 940 (Hoechst Gosei K.K.) was coated with the coating material prepared by using the aqueous dispersion of Application Example 1 using an applicator so that a 40 μm -thick coating film was obtained. After it was dried for 2 weeks at room temperature, 25 small squares separated at 2-mm intervals were made based on the method described in JIS K 5400 and then a tape-peeling test was carried out. The number of squares remaining was counted.

[0089]

Carbon staining: As in the adhesion test, a plate was prepared. Then the plate was coated uniformly with a 3 % concentration of carbon dispersed in ionized water using an airless spray gun. After drying at 60°C for 2 h, the carbon on the surface of the coating film was washed with running water using a brush and the ΔE of the coated plate after the drying was measured. The ΔE indicates the color difference of the coated plate and it was measured with a color-difference meter (Suga Shikenki Co., Ltd.). The results were evaluated using the following criteria.

- A $\Delta E < 5$
- B ΔE is 5-10
- C ΔE is 10-20
- D $\Delta E > 20$

[0090]

Boiling water resistance: After immersion in boiling water for 6 h, changes in the surface of the coating were visually observed and were evaluated using the following criteria.

- A no change
- B blisters occur
- C reduction of gloss of the coating film

[0091]

Solvent resistance: A film prepared from the aqueous dispersion was immersed in xylene at 25°C for one day. Then the amount of the xylene absorbed by the film was measured and the percentage of the change of weight of the film compared with the weight of the film before immersion in xylene was calculated.

- A solvent absorption less than 100 wt%
- B solvent absorption is 100-200 wt%,
- C solvent absorption is greater than 200 wt% (including the case of dissolution of the film.

[0092]

Weather resistance (accelerated weathering test): The test plate used for the above-mentioned gloss measurement, which was an aluminum plate coated with a 20 μm -thick coating using an applicator, was exposed for 1000 h to an Aispali [transliteration] UV tester (SUV) (Iwasaki Denki Co., Ltd.) and then the gloss was measured and the percentage to the initial gloss was expressed as gloss retention (%). The plates coated with (1) acrylic scaler and (2) elastic acrylic sealer which were prepared during the adhesion test were exposed to the SUV for 1000 h, then the adhesion (the adhesion after accelerated weathering test in Table III) was measured using the same method as that used above.

[0093]

The results are shown in Table II and Table III.

[0094]

Application Examples 2-14

The monomer mixtures, hydrazine derivatives, and aqueous dispersions of Synthetic Examples shown in Table II were used to prepare aqueous dispersion compositions using the method described in Application Example 1 and then the methods of evaluation used in Application Example 1 were used for evaluations. The results are shown in Table II and Table III.

[0095]

Comparative Example I

45 g of 0.5 wt% of JS 2 (Sanyo Chemical Industries, Ltd.) aqueous solution was put in a 200 mL-capacity 4-necked flask equipped with an impeller, a condenser, and a thermometer. Then while it was agitated it was heated in a water bath and when the temperature reached 80°C, an emulsion prepared by emulsifying a mixture of 50 g of methyl methacrylate, 6.0 g of acetoacetoxyethyl methacrylate, 7.5 g of RS 30 (Sanyo Chemical Industries, Ltd.), and 1.5 g of isooctyl thioglycolate with 20 g of 0.5 wt% of a JS 2 (Sanyo Chemical Industries, Ltd.) aqueous solution was added dropwise over a period of 1 h. Immediately after the addition, 1 mL of 2 wt% aqueous ammonium persulfite solution was added to start the reaction. 3 h after the start of the reaction, the temperature of the reactor was raised to 85°C and after maintaining that temperature for 1 h it was cooled, and then after the pH was adjusted to 7 with aqueous ammonia, an amount of a 10% aqueous adipic acid dihydrazide solution was added to the aqueous dispersion which was a 1.0 molar equivalent hydrazine residue with respect to the active carbonyl group of AAEM, followed by filtering through a 300-mesh screen to give a bluish-white fluorine-containing copolymer aqueous dispersion composition.

[0096]

A coating material was prepared using the thus-obtained aqueous dispersion composition as in Application Example I and the evaluation results are shown in Table II and Table III.

[00971]

Comparative Examples 2-7

The monomer mixtures, hydrazine derivatives, and aqueous dispersions of the synthetic examples in Table II were used for coating materials as in Application Example 1 and the evaluation results are shown in Table II and Table III.

[0098]

The aqueous dispersion composition in Comparative Example 2 was prepared without using an ethylenically unsaturated monomer and hydrazine derivative, the aqueous dispersion composition in Comparative Example 3 was prepared without using an ethylenically unsaturated monomer, the aqueous dispersion composition in Comparative Example 4 was prepared wherein the amount of adipic acid dihydrazide added was such that more than one molar equivalent of hydrazine residue with respect to the active carbonyl group of AAEM was added, the aqueous dispersion composition in Comparative Example 5 was prepared using less than 20 parts of monomer based on 100 parts of fluorine-containing copolymer, the aqueous dispersion composition in Comparative Example 6 was prepared using greater than 100 parts of monomers

based on 100 parts of fluorine-containing copolymer, and the aqueous dispersion composition in Comparative Example 7 was prepared using the method of Application Example 1 except that no hydrazine derivative was used.

[0099]

Table II

① 実 施 例														② 比 較 例						
③ 実施例および比較例番号		1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7
④ 合成例番号		1	1	1	1	1	1	1	2	3	4	5	6	-	1	1	1	1	1	1
⑤ 単量体重量部		43	43	43	43	43	20	99	43	43	43	43	43	100	43	43	43	17	110	43
⑥ 単量体(重量割合)	(b) *1 EHA *4				20								40	40						
	(c) *2 MMA *5	95	95	95	75	95	99.9	80	95	95	95	95	55	55	100	100	95	95	95	95
	(d) *3 AAEM *6	5	5	5	5		0.1	20	5	5	5	5	5	5			5	5	5	5
	AL *7					5														
⑦ アジピン酸ジドデカノール		1.0	0.02	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0	1.0	1.3	0.5	0.5	0
⑧ 水性分散液物	⑨ 固形分濃度(重量%)	47	47	47	47	47	43	51	47	40	40	34	58	50	47	47	47	42	53	47
	⑩ 平均粒子径(μ m)	0.16	0.16	0.16	0.16	0.16	0.14	0.18	0.17	0.13	0.16	0.17	0.22	0.15	0.16	0.16	0.16	0.14	0.20	0.16
	⑪ 最終成膜温度($^{\circ}$ C)	38	38	38	29	39	32	52	39	36	37	33	42	36	38	38	39	35	52	38

- Key: 1 Application Example
 2 Comparative Example
 3 No. of Application Example and Comparative Example
 4 No. of Synthetic Example
 5 Parts by weight of monomer
 6 Ratio of monomers in monomer mixture (wt%)

- 7 Amount of adipic acid dihydrazide
 8 Aqueous dispersion composition
 9 Concentration of solid matter (wt%)
 10 Average particle size
 11 Minimum film-forming temperature*

[0100]

Table III

		① 実 施 例												② 比 較 例							
③ 実施例および比較例番号		1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	
④ 塗膜特性	低温成膜性 ⑤	A	A	A	A	A	B	B	A	A	A	A	B	A	A	A	A	C	C	A	
	光沢 ⑥	68	74	73	74	73	63	76	54	55	61	61	51	78	76	72	62	54	57	74	
	鉛筆硬度 ⑦	H	HB	H	F	H	HB	H	F	F	F	F	F	HB	B	B	HB	B	H	B	
	密着性 ⑧	25	25	25	25	25	25	25	25	25	25	25	21	25	11	12	25	9	25	13	
	カーボン汚染性 ⑨	A	A	A	A	A	B	A	A	A	A	A	B	B	C	C	B	C	B	C	
	耐沸騰水性 ⑩	A	A	A	A	A	B	B	A	A	A	A	B	B	C	C	A	B	B	C	
塗膜特性	耐溶剤性 ⑪	A	B	A	A	A	B	A	A	A	A	A	A	A	C	C	A	B	A	C	
	耐候性 ⑫	87	94	92	91	92	82	75	72	73	82	84	71	13	90	86	65	66	62	89	

- * 1: Acrylic acid alkyl ester
 2: Methacrylic acid alkyl ester
 3: Ethylenically unsaturated monomer
 4: Ethylhexyl acrylate
 5: Methyl methacrylate
 6: Acetoacetoxyethyl methacrylate
 7: Acrolein
 8: Molar equivalent of hydrazine residue of adipic acid dihydrazide with respect to the active carbonyl group.

Key:	1	Application Example
	2	Comparative Example
	3	No. of Application Example and Comparative Example
	4	Characteristics of coating film
	5	Low-temperature film formability
	6	Gloss
	7	Pencil hardness
	8	Adhesion
	9	Carbon staining
	10	Boiling water resistance
	11	Solvent resistance
	12	Weather resistance

[0101]

Effect of the invention

According to the fluorine-containing polymer aqueous dispersion compositions of the present invention, coating films with excellent low-temperature film formability, external appearance, strength, stain resistance, boiling water resistance, solvent resistance, weather resistance, and adhesion to substrates can be provided.

[0102]

According to aqueous coating materials containing the fluorine-containing polymer aqueous dispersion compositions of the present invention, coating films with excellent low-temperature film formability, external appearance, strength, stain resistance, boiling water resistance, solvent resistance, weather resistance, and adhesion to substrates can be provided.

[0103]

Coated products obtained by coating substrates with the above-mentioned aqueous coating materials have coating films with excellent low temperature film formability, external appearance, strength, stain resistance, boiling water resistance, solvent resistance, weather resistance, and adhesion to substrates, therefore the coated products can be used in many fields.